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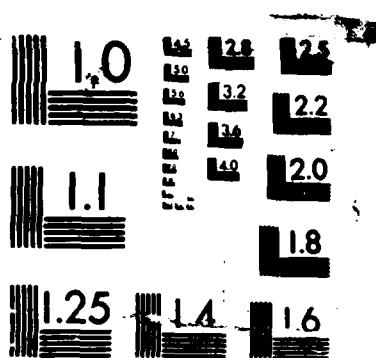
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TECHNICAL REPORT NO. 128

Cupraboranes Containing a *clos*-Cu(I)C₂B₉ Geometry.

Synthesis and Structure of [(PPh₃)CuC₂B₉H₁₁]⁺ and [(PPh₃)₂Cu₂(μ-H)₂C₂B₉H₉].

by

Youngkyu Do, Han Chyul Kang, Carolyn B. Knobler and M. Frederick Hawthorne*

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crystallizes in the monoclinic space group $P2_1/n$, with $a = 11.507(1)$, $b = 14.772(1)$, $c = 30.751(2)$ Å, $\beta = 90.284(2)^\circ$, $Z = 4$.

Cupracarboranes Containing a *closo*-Cu(I) C_2B_9 Geometry.
Synthesis and Structure of
[(PPh₃)CuC₂B₉H₁₁]⁻ and [(PPh₃)₂Cu₂(μ -H)₂C₂B₉H₉].



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Abstract

The reaction chemistry of [*nido*-7,8-C₂B₉H₁₁]²⁻ with copper(I) has been examined to provide anaerobic synthetic routes to two novel phosphinocupracarboranes, [(PPh₃)CuC₂B₉H₁₁]⁻ and [(PPh₃)₂Cu₂(μ -H)₂C₂B₉H₉]. The structural analysis reveals that both cupracarboranes adopt a *closo* geometry for the d¹⁰ MC₂B₉ icosahedra. Two copper(I) centers of the homodinuclear complex are incorporated into one carborane cage via the open pentagonal C₂B₃ face and two B-H-Cu bridges. Both bridging BH units stem from the upper pentagonal belt resulting in the interatomic Cu(I)-Cu(I) distance of 2.576(1) Å. The relatively close Cu(I)-Cu(I) proximity can be ascribed to a metal-metal interaction and the dinuclear cupracarborane can be viewed as a zwitterionic salt which upon dissolution remains intact while exhibiting fluxional behavior. The nature of these fluxional processes has been explored by variable temperature multinuclei FTNMR spectroscopy.

[(PPh₃)₂Cu₂(μ -H)₂C₂B₉H₉] crystallizes in the monoclinic space group P2₁/n, with $a = 10.005(2)$, $b = 20.693(4)$, $c = 18.998(3)$ Å, $\beta = 92.664(6)^\circ$, $Z = 4$. PPN[(PPh₃)CuC₂B₉H₁₁] crystallizes in the monoclinic space group P2₁/n, with $a = 11.507(1)$, $b = 14.772(1)$, $c = 30.751(2)$ Å, $\beta = 90.284(2)^\circ$, $Z = 4$.

Cupracarboranes Containing a *clos*-Cu(I)C₂B₉ Geometry. Synthesis and Structure of [(PPh₃)CuC₂B₉H₁₁]⁺ and [(PPh₃)₂Cu₂(μ -H)₂C₂B₉H₉].

Sir:

An additional manifestation of the versatile electron donor ability of [*nido*-7,8-C₂B₉H₁₁]²⁻ (**1**)¹ in metallacarborane chemistry has recently appeared in the form of polynuclear metallacarboranes involving exopolyhedral boron-hydride-metal three-center, two-electron linkages.^{2,3} While the bridge bonding mode **I** is the most usual pattern encountered in polynuclear metal complexes of **1**, the unit **II** has only been realized in the bimetallic aluminacarborane, *commo*-3,3'-Al[(*exo*-8,9-(μ -H)₂Al(C₂H₅)₂-3,1,2-AlC₂B₉H₉)-(3',1',2'-AlC₂B₉H₁₁)] (**2**),^{3c,4} in which the bridging BH units stem from the upper and



lower pentagonal belts of one dicarbollide cage. As part of the investigation into the extended use of **1** in the synthesis of novel metallacarboranes containing metal-hydride-boron bridge bonds, the reaction chemistry of **1** with copper(I) has been examined.⁵

Routes to two novel phosphinocupracarboranes have recently been discovered. Depending on the absence or presence of (PPN)⁺Cl⁻ (PPN⁺ = *bis*(triphenylphosphoranylidene)ammonium cation), the dithallium salt⁶ of **1** reacts with triphenylphosphine-substituted

copper(I) chlorides (L_nCuCl , $n = 1,2$) to form either dinuclear *closo*-[*exo*-4,8-(μ -H)₂Cu-(PPh₃)₃-(PPh₃)-3,1,2-CuC₂B₉H₉] (3; white; 79%) or mononuclear (PPN)[*closo*-3-(PPh₃)₃-3,1,2-CuC₂B₉H₁₁] [(PPN)·4; off-white; 84%]. Both compounds were characterized by single-crystal X-ray analyses⁷ as well as other means.⁸

The crystal structure of 3 consists of two enantiomers related by an inversion center to form the racemic system. The structure of 3, shown in Figure 1, contains two copper(I) centers

[Figure 1]

which are incorporated into one carborane cage via the open pentagonal C₂B₃ face and two B-H-Cu bridges as in mode II. Both bridging BH units originate from the upper pentagonal belt, in contrast to 2, such that the plane of Cu(01)-B(04)-B(08) forms a dihedral angle of 40.9° with the pentagonal C₂B₃ plane (± 0.016 Å) and the interatomic distance between two copper(I) ions of formal d¹⁰ configuration is 2.576(1) Å. This structural situation raises at least two engaging questions as to the geometry of the polyhedral framework of the Cu(03)C₂B₉ fragment and the extent of Cu(I)-Cu(I) interaction.

The structure of metallacarboranes containing electron-rich late transition metal ions has been described in terms of molecular distortions such as the slipping,^{9,10} folding¹⁰ and tilting^{5,11} distortions. The parameters which are associated with these molecular distortions remain useful for descriptive purposes, but do not always delineate the electron count of the polyhedral framework of the MC₂B₉ cages. Nevertheless, the structural analysis favors *closo* geometry for the Cu(03)C₂B₉ cage of 3. In 3, the lower B₅ plane is nearly planar (± 0.004 Å) while the upper C₂B₃ plane experiences a minor distortion with 2.3° and 1.1° for the folding parameters¹⁰ θ and ϕ , respectively. The displacement of Cu(03) from the perpendicular passing through the centroid of the lower B₅ plane, known as the slipping parameter Δ ,¹⁰ is calculated to be 0.25 Å. These values for the distortion parameters fall into the range observed in *closo* icosahedral metallacarboranes¹² rather than slipped metallacarboranes.¹³ The interaction of copper with the cage via the open C₂B₃ face in 3 is typical of *closo*-MC₂B₉ complexes so far

structurally characterized,^{14,15} with a mean M-C/M-B distance ratio (1.06) close to unity. The anionic *closo*-[LCuC₂B₉H₁₁]⁻ fragment of 3 can be synthesized as a separate, isolated entity. The compound (PPN)·4 is such an example and the structure of 4, as displayed in Figure 2, also

[Figure 2]

adopts *closo* geometry.¹⁶ The *closo* geometry for the d¹⁰ MC₂B₉ icosahedra, in both 3 and 4, seems to be unusual since a progressive opening of the MC₂B₉ metallacarborane cage has been pointed out⁵ as a trend in the structural changes for the isoelectronic 18-electron series [Re(CO)₃C₂B₉H₁₁]⁻,^{12a} [Au(S₂CNEt₂)C₂B₉H₁₁],^{11,13c} [Hg(PPh₃)C₂B₉H₁₁]⁻,^{5,17} and [Tl-C₂B₉H₁₁]⁻.^{17,18} However this geometry has been anticipated as a possible structure for (PPh₃)CuC₂B₉H₁₀(C₅H₅N).⁵ by analogy with the known η⁵ structure of (PPh₃)Cu(C₅H₅).¹⁹

A range of Cu-Cu distances from 2.35 Å to about 3.6 Å is found in polynuclear copper(I) compounds.²⁰ MO analyses performed with Cu_nⁿ⁺ (n = 2,4) at the extended Hückel level of approximation supports the existence of a soft and attractive Cu(I)-Cu(I) interaction, overlaid upon the requirements of the bridging ligand set.^{20b} In [Cu₂(tmen)₂(μ-CO)(μ-PhCO₂)]⁺ the bridging ligand stereochemistry dominates, resulting in the very short Cu(I)-Cu(I) distance of 2.419(2) Å,^{20c} whereas in 3 the stereochemical requirements of the bridging ligand (1) are likely to be minimal since the elevation angles of the hydrogen substituents in the MC₂B₉H₁₁ cages are not restricted to that of a regular icosahedron.^{10b} Thus the relatively close Cu(I)-Cu(I) proximity in 3 can be considered to be a consequence of a metal-metal interaction similar to that found in Fe₂(CO)₆C₄(CH₃)₂(OH)₂²¹ and its homologues.²²

Although the isolation of the anionic compound 4 supports the zwitterionic nature of 3, (PPN)·4 does not convert to 3 in the presence of LCuCl. The dinuclear structural integrity of 3 remains intact upon dissolution although fluxional motions become operative above 253 K since coalescence occurs at this temperature as observed by variable temperature ³¹P{¹H} FTNMR spectroscopy.^{8a} At 203 K, the two phosphorus nuclei of 3 are distinguishable while the two

CH hydrogens of the carborane cage remain indistinguishable in ^1H NMR, indicating that at least one kind of fluxional motion is still present at this temperature. The evidence at hand does not unequivocally reveal the nature of the fluxional processes.

Acknowledgment. The authors gratefully acknowledge the support of this work by the Office of Naval Research. We also would like to thank Dr. A. Varadarajan for informative discussions.

Supplementary Material Available: Details of crystallographic data collection, tables of positional and thermal parameters and interatomic distances and angles (15 pages). Ordering information is given on any current masthead page.

References and Footnotes

1. Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjer, M.; Warren, Jr., L. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.
2. Green, M.; Howard, J. A. K.; James, A. P.; Jelfs, A. N. de M.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1778.
3. a) Baker, R. T.; King, III, R. E.; Knobler, C. B.; O'Con, C. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 8266. b) Behnken, P. E.; Marder, T. B.; Baker, R. T.; Knobler, C. B.; Thompson, M. R.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1985**, *107*, 932. c) Rees, Jr., W. S.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5367. d) Do, Y.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1987**, *109*, 1853.
4. The bridging unit **II** is not uncommon in metallaboranes or in mononuclear metallacarboranes. Examples include the following: (a) $\text{Cu}_2(\text{PPh}_3)_4(\text{B}_{10}\text{H}_{10})$; Gill, J. T.; Lippard, S. J. *Inorg. Chem.* **1975**, *14*, 751. (b) $\text{HMn}_3(\text{CO})_{10}(\text{BH}_3)_2$; Kaesz, H. D.; Fellman, W.; Wilkes, G. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1965**, *87*, 2753. (c) *exo-nido*-Phosphinerhodacarboranes; Knobler, C. B.; Marder, T. B.; Mizusawa, E. A.; Teller, R. G.; Long, J. A.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2990.
5. The derivative chemistry of **1** with Cu(I) has remained virtually unexplored. The only compound reported to date is $[(\text{PPh}_3)\text{CuC}_2\text{B}_9\text{H}_{10}(\text{NC}_5\text{H}_5)]$ for which X-ray structural data are not available: Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1979**, 619.
6. Spencer, J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1178.

7. a) Suitable crystals of **3** and (PPN, **4** were grown from dichloromethane/ether. Diffraction data on both compounds were collected at 25 °C on a locally built automated diffractometer, using Mo K α radiation, to a maximum 2 θ of 50°. The structures were solved by a combination of conventional Patterson, Fourier and least-squares techniques.

b) Crystallographic data for **3** [(PPN·**4**]: $a = 10.005(2)$ [11.507(1)] Å, $b = 20.693(4)$ [14.772(1)] Å, $c = 18.998(3)$ [30.751(2)] Å, $\beta = 92.664(6)$ [90.284(2)] °, $V = 3924$ [5227] Å³; space group, $P2_1/n$ [$P2_1/n$]; unique data ($I > 3 \sigma(I)$), 5071 [4831]; R (R_w), 4.5 (6.1) [6.4 (7.5)] %. All calculations were performed on the DEC VAX 750 of the J. D. McCullough Crystallography Laboratory using the UCLA Crystallography Package.

8. (a) Data for **3**: Anal. Calcd. (Found): C, 58.21 (57.94); H, 5.27 (5.10); B, 12.41 (11.79); Cu, 16.21 (16.11); P, 7.90 (7.44). IR spectrum (KBr): $\nu_{BH} = 2559, 2498$; $\nu_{BHCu} = 2327$ (weak and broad) cm⁻¹. Chemical shifts upfield of the reference are designated as negative. $^{11}B\{^1H\}$ NMR (160.463 MHz) in dichloromethane, referenced to external $BF_3 \cdot OEt_2$ in C_6D_6 : -17.4, -19.7, -22.5, -24.2, -29.7, -31.2 ppm. 1H NMR (200.133 MHz) in CD_2Cl_2 (referenced to residual solvent protons = 5.32 ppm): 2.01 (carborane CH). $^{31}P\{^1H\}$ NMR (81.02 MHz) (CD_2Cl_2 ; referenced to 85% H_3PO_4): 7.9 (above 253 K); 4.7 and 10.1 ppm (at 203 K). (b) Data for **4**: Anal. Calcd. (Found): C, 67.48 (67.44); H, 5.66 (5.75); B, 9.76 (9.57); Cu, 6.37 (6.26); N, 1.41 (1.36); P, 9.32 (9.39). IR spectrum (KBr): $\nu_{BH} = 2571, 2537, 2488, 2418$ cm⁻¹. $^{11}B\{^1H\}$ NMR (CH_2Cl_2): -17.2, -20.2, -22.1, -23.0, -24.9, -34.9 ppm. 1H NMR in CD_2Cl_2 : 1.57 ppm (carborane CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 20.6 (PPN), 7.8 (PPh₃) ppm.

9. a) Warren, Jr., L. F.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 4823; **1970**, *92*, 1157. b) Wing, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 5599; **1968**, *90*, 4828.

10. a) Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Chem. Commun.* **1977**, 605. b) Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Dalton Trans.* **1978**, 1363.

11. Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* 1978, 303.
12. a) $\theta = 1.4^\circ$, $\phi = 1.2^\circ$, $\Delta = 0.05 \text{ \AA}$ for $[\text{Re}(\text{CO})_3\text{C}_2\text{B}_9\text{H}_{11}]^-$. Zalkin, A.; Hopkins, T. E.; Templeton, D. H. *Inorg. Chem.* 1966, 5, 1189. b) $\Delta = 0.05 \text{ \AA}$ for $[(\text{PPh}_3)_2\text{Rh-C}_2\text{B}_9\text{H}_{11}]^-$. Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* 1985, 24, 2688. c) $\theta + \phi = 9.7^\circ$, $\Delta = 0.26 \text{ \AA}$ for $(\text{PMe}_3)_2\text{PdC}_2\text{B}_9\text{H}_{11}$. Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* 1978, 322.
13. a) $\theta + \phi = 14.5^\circ$, $\Delta = 0.52 \text{ \AA}$ for $[\text{C}_2\text{H}_4(\text{NMe}_2)_2]\text{PdC}_2\text{B}_9\text{H}_{11}$. Reference 12c. b) $\theta = 4.7^\circ$, $\phi = 4.4^\circ$, $\Delta = 0.42 \text{ \AA}$ for $(\text{PEt}_3)_2\text{PtC}_2\text{B}_9\text{H}_{11}$. Reference 10. c) $\theta = 7.7^\circ$, $\phi = 9.5^\circ$, $\Delta = 0.5 \text{ \AA}$ for $(\text{S}_2\text{CNEt}_2)\text{AuC}_2\text{B}_9\text{H}_{11}$. Reference 11 and Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* 1976, 1019.
14. The mean M-C/M-B distances ratio for the *clos*o icosahedral metallacarboranes excluding the *commo* systems: a) 0.97 in $(\text{PPh}_3)_2(\text{HSO}_4)\text{RhC}_2\text{B}_9\text{H}_{11}$. Kalb, W. C.; Teller, R. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1979, 101, 5417. b) 0.99 in $(\text{PPh}_3)_2(\text{Br}_2)\text{RhC}_2\text{B}_9\text{H}_{11}$. Zheng, L.; Baker, R. T.; Knobler, C. B.; Walker, J. A.; Hawthorne, M. F. *Inorg. Chem.* 1983, 22, 3350. c) 0.99 in $[\text{Re}(\text{CO})_3\text{C}_2\text{B}_9\text{H}_{11}]^-$. Reference 12a. d) 0.99 in $(\text{PPh}_3)_2\text{HRhC}_2\text{B}_9\text{H}_{11}$. Hardy, G. E.; Callahan, K. P.; Strouse, C. E.; Hawthorne, M. F. *Acta Cryst.* 1976, B32, 264. e) 1.0 in $(\text{PPh}_3)(\text{NO}_3)\text{RhC}_2\text{B}_9\text{H}_{11}$. Demidowicz, Z.; Teller R. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* 1979, 831. f) 1.01 in $[(\text{PPh}_3)_2\text{RhC}_2\text{B}_9\text{H}_{11}]^-$. Reference 12b. g) 1.02 in $(\text{PPh}_3)(\text{CO})\text{RhC}_2\text{B}_9\text{H}_{10}(\text{C}_5\text{H}_5\text{N})$. Teller, R. G.; Wilczynski, J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* 1979, 472. h) 1.02 and 1.03 in $[(\text{PPh}_3)\text{RhC}_2\text{B}_9\text{H}_{11}]_2$. Reference 3a,b. i) 1.08 in $(\text{PMe}_3)_2\text{PdC}_2\text{B}_9\text{H}_{11}$. Reference 12c.

15. The mean M-C/M-B distances ratio for the slipped icosahedral metallacboranes excluding the *commo* systems: a) 1.13 in $(PEt_3)_2PtC_2B_9H_{11}$. Reference 13b. b) 1.20 in $[C_2H_4 \cdot (NMe_2)_2]PdC_2B_9H_{11}$. Reference 13a. c) 1.26 in $(S_2CNEt_2)AuC_2B_9H_{11}$. References 11 and 13c.
16. For **4**, the values of θ , ϕ , Δ and the M-C/M-B ratio are 2.4° , 1.6° , 0.21 \AA and 1.07, respectively.
17. Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1977**, 737.
18. Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *Acta Cryst.* **1978**, *B34*, 2373.
19. Cotton, F. A.; Takats, J. *J. Am. Chem. Soc.* **1970**, *92*, 2353.
20. a) Reference 3d and references cited therein. b) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187 and references cited therein. c) Pasquali, M.; Floriani, C.; Gaetain-Maufredotti, A.; Guastini, C. *J. Am. Chem. Soc.* **1981**, *103*, 185.
21. Hock, A. A.; Mills, O. S. *Acta Cryst.* **1961**, *14*, 139.
22. a) Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 5068. b) Dettlaf, G.; Weiss, E. *J. Organometal. Chem.* **1976**, *108*, 213.

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Figure Captions

Figure 1. Structure of $[(\text{PPh}_3)_2\text{Cu}_2(\mu\text{-H})_2\text{C}_2\text{B}_9\text{H}_9]$ (3) showing atom-labeling scheme. Labeling of phenyl rings and all hydrogen atoms except the bridging hydrides have been omitted for clarity. Selected values of interatomic distances (\AA) and angles (deg): Cu(01)-Cu(03), 2.576(1); Cu(01)-P(02), 2.197(1); Cu(03)-P(01), 2.164(1); Cu(03)-C(C_2B_3 face), 2.331(4), 2.280(4); Cu(03)-B(C_2B_3 face), 2.226(5), 2.164(5), 2.140(5); Cu(01)-B(C_2B_3 face), 2.173(5), 2.210(4); P(01)-Cu(03)-B(10), 162.5(1).

Figure 2. Structure of $[(\text{PPh}_3)\text{CuC}_2\text{B}_9\text{H}_{11}]^-$ (4) showing atom-labeling scheme. Selected values of interatomic distances (\AA) and angles (deg): Cu(03)-P(01), 2.147(2); Cu(03)-C(C_2B_3 face), 2.316(6), 2.317(6); Cu(03)-B(C_2B_3 face), 2.181(7), 2.167(7), 2.116(7); P(01)-Cu(03)-B(10), 162.9(1).

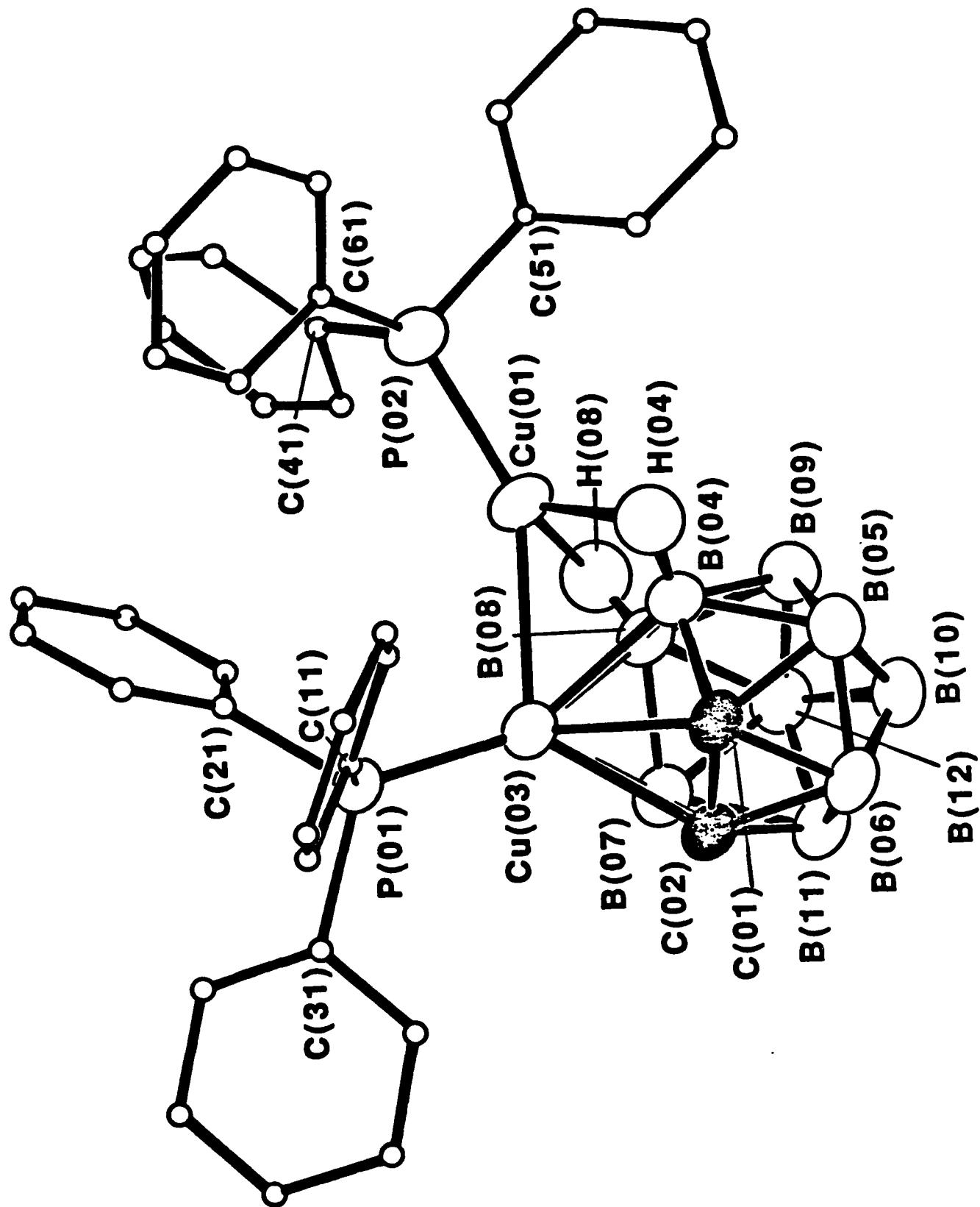
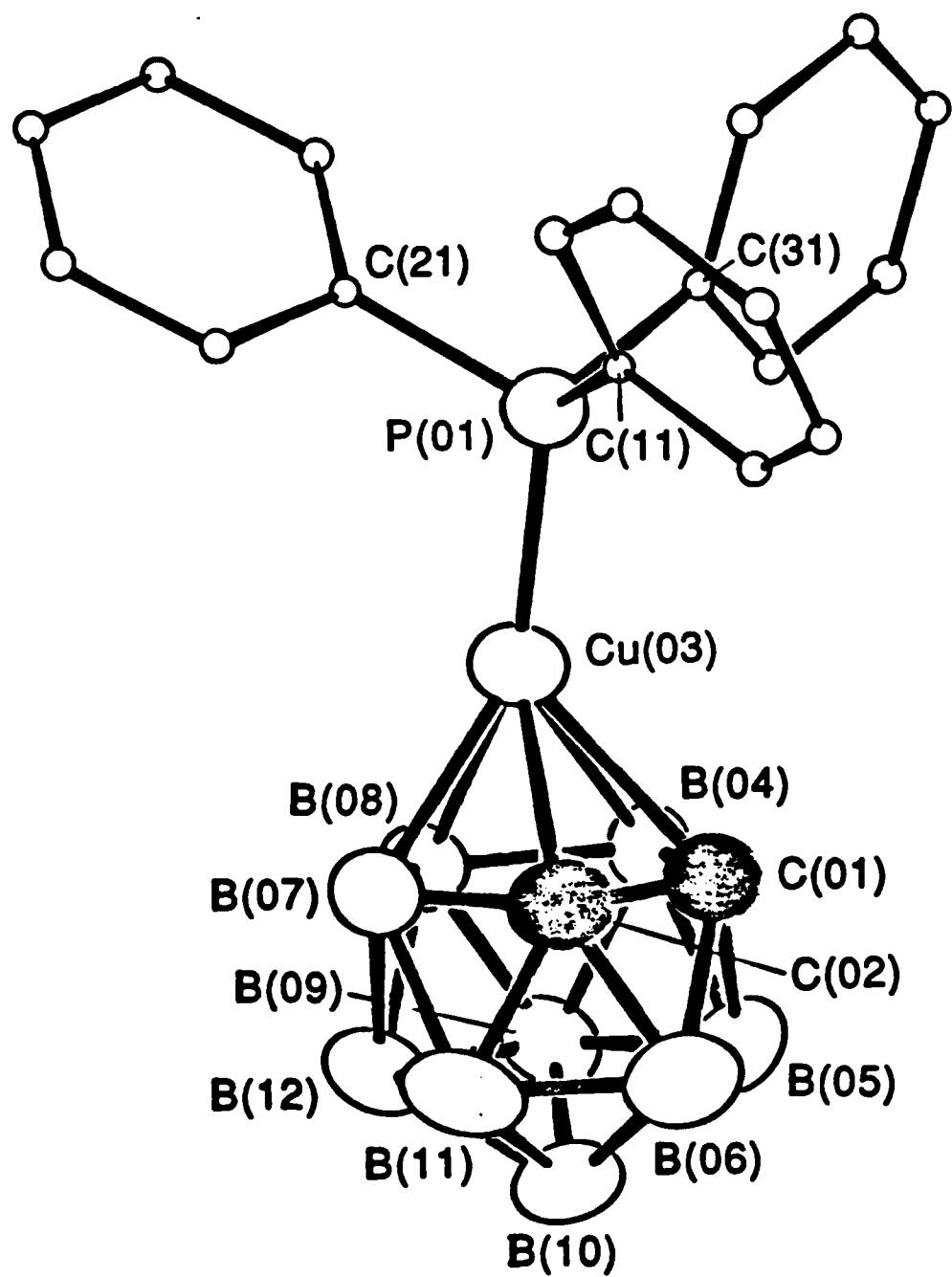


Fig #2



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